

DERWENT-ACC-NO: 1994-114831  
DERWENT-WEEK: 199414  
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TITLE: Impact resistant composite board and having good bending strength -  
consists of brittle baseboard, 1st FRP layer contg monoaxially orientated  
fibres and 2nd FRP layer comprising reinforced fibre-woven cloth and  
impregnating resin

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PRIORITY-DATA: 1992JP-0244164 (August 20, 1992)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	
PAGES	MAIN-IPC		
JP 06064076 A	March 8, 1994	N/A	006
B32B 005/00			

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO
APPL-DATE		
JP06064076A	N/A	1992JP-0244164
August 20, 1992		

INT-CL (IPC): B32B005/00; B32B017/04 ; B32B019/00 ;  
B44C003/02

ABSTRACTED-PUB-NO: JP06064076A

BASIC-ABSTRACT: The composite board comprises (I) a brittle baseboard; (II) a first FRP (fibre-reinforced plastic) layer comprising reinforcing fibre orientated at least mon-directionally and impregnated resin; and (III) a second FRP layer comprising reinforcing fibre woven into cloth and impregnated resin.

Also claimed is formation of a composite board by (a) forming a brittle baseboard; (b) forming a reinforcing fibre sheet prepd. by adhesively bonding a base sheet in the form of woven cloth with monodirectionally orientated fibre; (c) positioning the reinforcing fibre sheet onto the surface of the brittle

baseboard and (c) coating the matrix resin onto the outer surface of the reinforcing fibre sheet to impregnate the matrix resin into the reinforcing fibre to harden the resin.

The brittle board is, e.g., a ceramic board, thin marble board, tile or thin concrete board.

ADVANTAGE - Composite board has a sufficient impact resistance and bending strength even when the brittle board has a thickness of upto 5 mm. Furthermore, it has improved workability and reduced wt.

CHOSEN-DRAWING: Dwg.0/5

TITLE-TERMS:

IMPACT RESISTANCE COMPOSITE BOARD BEND STRENGTH CONSIST BRITTLE  
BASEBOARD FRP  
LAYER CONTAIN MONOAXIAL ORIENT FIBRE FRP LAYER COMPRISE  
REINFORCED FIBRE WOVEN  
CLOTH IMPREGNATE RESIN

DERWENT-CLASS: A32 A94 P73 P78

CPI-CODES: A11-B09C; A12-S08A;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

017 ; P0000 ; L9999 L2391 ; L9999 L2073 ; M9999 M2073

Polymer Index [1.2]

017 ; ND01 ; ND07 ; Q9999 Q7818\*R ; B9999 B4159 B4091 B3838  
B3747

; K9892 ; B9999 B4148 B4091 B3838 B3747 ; K9483\*R ; K9574  
K9483

; K9698 K9676 ; Q9999 Q7249 ; N9999 N6042\*R ; N9999 N5721\*R ;  
K9494

K9483 ; K9610 K9483 ; B9999 B5243\*R B4740 ; B9999 B3623 B3554  
;

B9999 B4842 B4831 B4740

Polymer Index [1.3]

017 ; A999 A419 ; S9999 S1070\*R ; B9999 B5174 B5152 B4740

Polymer Index [1.4]

017 ; A999 A419 ; S9999 S1194 S1161 S1070

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials: 0011

0229  
0231  
2020  
2198  
2212  
2215  
2220  
2488  
2491  
2493  
2547  
2560  
2617  
2632  
2646  
2654  
2726  
2729  
2836  
3267

Multipunch Codes: 017

03-  
04-  
231  
308  
309  
359  
38&  
437  
443  
445  
446  
46&  
473  
477  
494  
512  
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581  
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722  
723

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1994-052947

Non-CPI Secondary Accession Numbers: N1994-090149

(19)日本国特許庁(JP)

(12)公開特許公報(A)

(11)特許出願公開番号

特開平6-64076

(43)公開日 平成6年(1994)3月8日

(51)Int.Cl. <sup>5</sup>	識別記号	庁内整理番号	F I	技術表示箇所
B 3 2 B 5/00	A	7016-4F		
17/04	Z			
19/00				
B 4 4 C 3/02	A	9134-3K		

審査請求 未請求 請求項の数3(全 6 頁)

(21)出願番号 特願平4-244164

(22)出願日 平成4年(1992)8月20日

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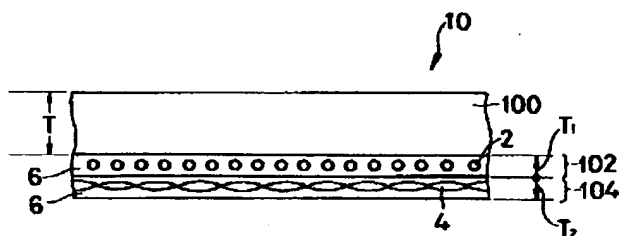
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(54)【発明の名称】 複合板材及びその製造方法

(57)【要約】

【目的】 例え脆性板材の厚さを5mm以下とした場合においても、十分な耐衝撃性及び曲げ強度を発揮することができ、取扱い性の向上及び重量の軽減を図ることのできる複合板材及びその製造方法を提供する。

【構成】 セラミック板材、大理石などの脆性板材100の表面或は裏面に、第1の繊維強化樹脂層102及び第2の繊維強化樹脂層104が積層される。第1の繊維強化樹脂層102は、一方向に配列された強化繊維2に樹脂(マトリクス樹脂)6を含浸して形成され、第2の繊維強化樹脂層104は、クロス(織物)に織り込まれた強化繊維4に樹脂(マトリクス樹脂)6を含浸して形成される。



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## 【特許請求の範囲】

【請求項1】 板状の脆性基板の一侧に、少なくとも、一方向に配列された強化繊維に樹脂が含浸された第1の繊維強化樹脂層と、クロスに織り込まれた強化繊維に樹脂が含浸された第2の繊維強化樹脂層とが積層されたことを特徴とする複合板材。

【請求項2】 (a) 板状の脆性基板を準備すること、  
(b) クロスに織り込まれた強化繊維からなる支持体シートに、一方向に配列された強化繊維を接着剤層を介して接着して構成される強化繊維シートを準備すること、  
(c) 前記脆性基板の一侧面に前記強化繊維シートを位置せしめること、  
(d) 前記強化繊維シートの外側面にマトリクス樹脂を塗布し、そして、前記支持体シート及び前記強化繊維にマトリクス樹脂を含浸させ、硬化すること、を特徴とする複合板材の製造方法。

【請求項3】 (a) 板状の脆性基板を準備すること、  
(b) クロスに織り込まれた強化繊維からなる支持体シートに、一方向に配列された強化繊維を接着剤層を介して接着して構成される強化繊維シートを準備すること、  
(c) 前記強化繊維シートの片面にマトリクス樹脂を塗布した後、この面が前記脆性基板の一侧面に対面するようにして、前記脆性基板に前記強化繊維シートを貼り付けること、  
(d) 前記強化繊維シートの外側面にマトリクス樹脂を塗布し、そして、前記支持体シート及び前記強化繊維にマトリクス樹脂を含浸させ、硬化すること、を特徴とする複合板材の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、セラミック板材、大理石などの自然石の薄板、タイル、コンクリート薄板などの脆性板材の表面或は裏面に繊維強化樹脂層を貼着した複合板材に関するものであり、耐衝撃性、曲げ強度が大きく、又板材の厚みが薄く、より重量を軽減することができ、建物の内装、外装材、床材、テーブルの天板、ドアなどに好適に使用することができる。

## 【0002】

【従来の技術】近年、セラミック板材、大理石などの自然石の薄板、タイル、コンクリート薄板などが建物の内装、外装材、床材、テーブルの天板、ドアなどとして使用されているが、これら材料は、比重が大であり重く、又、その価格も高い。そのために、重さを減らして取扱い性を向上させ、更には材料費、輸送コスト或は施工コストを低減するために、その厚さはできるだけ薄くすることが望まれている。しかしながら、厚さを薄くした場合には、脆く耐衝撃性が低くなり、その取扱いに相当の注意を払わねばならないという問題がある。

【0003】このような問題を解決するために、特開昭63-222850号公報には、厚さ10mm程度のこのような脆性板材の片面に、強化繊維としてガラス繊維テープに樹脂を含浸させて形成したFRPアブリゲテ

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ープを貼着した複合板材が提案されている。

## 【0004】

【発明が解決しようとする課題】しかしながら、本発明者らの研究実験の結果によると、この公開公報に開示するような構成の複合板材では、十分な耐衝撃性を得るには脆性板材の厚さは少なくとも10mm程度は必要とし、例えば脆性板材の厚さを5mm以下とした場合には、十分な耐衝撃性を得ることができないだけでなく、曲げ強度が著しく低下することを見出した。

【0005】従って、本発明の目的は、例え脆性板材の厚さを5mm以下とした場合においても、十分な耐衝撃性及び曲げ強度を発揮することができ、取扱い性の向上及び重量の軽減を図ることのできる複合板材及びその製造方法を提供することである。

## 【0006】

【課題を解決するための手段】上記目的は本発明に係る複合板材及びその製造方法によって達成される。要約すれば、本発明は、板状の脆性基板の一侧に、少なくとも、一方向に配列された強化繊維に樹脂が含浸された第1の繊維強化樹脂層と、クロスに織り込まれた強化繊維に樹脂が含浸された第2の繊維強化樹脂層とが積層されたことを特徴とする複合板材である。

【0007】斯かる複合板材は、(a) 板状の脆性基板を準備すること、(b) クロスに織り込まれた強化繊維からなる支持体シートに、一方向に配列された強化繊維を接着剤層を介して接着して構成される強化繊維シートを準備すること、(c) 前記脆性基板の一侧面に前記強化繊維シートを位置せしめること、(d) 前記強化繊維シートの外側面にマトリクス樹脂を塗布し、そして、前記支持体シート及び前記強化繊維にマトリクス樹脂を含浸させ、硬化すること、を特徴とする製造方法にて好適に製造することができる。

【0008】又、別法として、本発明の複合板材は、

(a) 板状の脆性基板を準備すること、(b) クロスに織り込まれた強化繊維からなる支持体シートに、一方向に配列された強化繊維を接着剤層を介して接着して構成される強化繊維シートを準備すること、(c) 前記強化繊維シートの片面にマトリクス樹脂を塗布した後、この面が前記脆性基板の一侧面に対面するようにして、前記脆性基板に前記強化繊維シートを貼り付けること、  
(d) 前記強化繊維シートの外側面にマトリクス樹脂を塗布し、そして、前記支持体シート及び前記強化繊維にマトリクス樹脂を含浸させ、硬化すること、を特徴とする製造方法にても好適に製造することができる。

## 【0009】

【実施例】次に、本発明に係る複合板材及びその製造方法について図面に即して更に詳しく説明する。

【0010】本発明の複合板材10は、例えば図1に図示されるように、セラミック板材、大理石などの自然石の薄板、タイル、コンクリート薄板などの板状の脆性基

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板、即ち、脆性板材100の表面或は裏面に、第1の繊維強化樹脂層102及び第2の繊維強化樹脂層104が積層される。脆性板材100は、その厚さ(T)は、製造し得る限りにおいて薄くすることができ、例えば、セラミック或は大理石からなる板材においては2~4mm程度にまで薄くしたものを使用することができる。

【0011】又、第1の繊維強化樹脂層102は、一方に配列された強化繊維2に樹脂(マトリクス樹脂)6を含浸して形成され、第2の繊維強化樹脂層104は、クロス(織物)に織り込まれた強化繊維4に樹脂(マトリクス樹脂)6を含浸して形成される。

【0012】前記第1の繊維強化樹脂層102に使用される強化繊維2としては、炭素繊維が最も好ましいが、例えば、ボロン繊維、ガラス繊維、アルミナ繊維、炭化珪素繊維、窒化珪素繊維などの無機繊維；アラミド繊維、ポリアリレート繊維、ポリエチレン繊維、ポリエステル繊維などの有機繊維；或は、チタン繊維、アモルファス繊維、ステンレススチール繊維などの金属繊維から選択される1種を用いて、或は、複数種からなるハイブリッドの形態にて使用することができる。又、前記第2の繊維強化樹脂層104に使用されるクロスの強化繊維4としては、炭素繊維、ガラス繊維、又はアラミド繊維、ポリアリレート繊維、ポリエチレン繊維、ポリエステル繊維などの有機繊維をクロスにしたものが好ましい。

【0013】第1及び第2の繊維強化樹脂層102、104にて強化繊維2、4に含浸されるマトリクス樹脂6は、通常同じ樹脂が使用され、例えば、エポキシ樹脂、不飽和ポリエステル樹脂、ポリウレタン樹脂、ジアリルフタレート樹脂、フェノール樹脂などの熱硬化性マトリクス樹脂が使用可能である。又、更に、硬化温度が50~200℃となるように、更に好ましくは常温にて硬化し得るように、硬化剤その他の付与剤、例えば可撓性付与剤などが適当に添加される。

【0014】好ましい一例を挙げれば、このマトリクス樹脂としてはエポキシ樹脂が好ましく、使用可能のエポキシ樹脂としては、例えば、(1)グリシジルエーテル系エポキシ樹脂(ビスフェノールA、F、S系エポキシ樹脂、ノボラック系エポキシ樹脂、臭素化ビスフェノールA系エポキシ樹脂)；(2)環式脂肪族エポキシ樹脂；(3)グリシジルエステル系エポキシ樹脂；(4)グリシジリアミン系エポキシ樹脂、テトラグリシジリアミノジフェニルメタン、トリグリシジール-p-アミノフェノールなど；(5)複素環式エポキシ樹脂；その他種々のエポキシ樹脂から選択される1種又は複数種が使用され、特に、ビスフェノールA、F、Sグリシジリアミン系エポキシ樹脂が好適に使用される。又、硬化剤としてはアミン系硬化剤、例えばジシアンジアミド(DICY)、ジアミノジフェニルスルホン(DDS)、ジアミノジフェニルメタン(DDM)；酸無水物系、例え

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ばヘキサヒドロ無水フタル酸(HHPA)、メチルヘキサヒドロ無水フタル酸(MHHPA)などが使用されるが、特にアミン系硬化剤が好適に使用される。

【0015】又、第1及び第2の繊維強化樹脂層102、104における強化繊維2、4とマトリクス樹脂6の配合割合は、任意に調整し得るが、通常、重量%で、強化繊維：マトリクス樹脂=20~70：80~30とされ、又、各繊維強化樹脂層102、104の厚さ(T<sub>1</sub>)、(T<sub>2</sub>)は、使用される強化繊維の直径程度の厚さにまで薄くし得るが、通常50~1000μm程度とされるであろう。

【0016】斯かる構成の本発明に係る複合板材10は、脆性板材100に、一方向配列強化繊維2を有する第1の繊維強化樹脂層102と、強化繊維クロス4を有する第2の繊維強化樹脂層104とが積層されているために、耐衝撃強度及び曲げ強度が著しく向上する。そのために、前述した特開昭63-222850号公報に記載されるような、厚さ10mm程度の脆性板材の片面に、強化繊維としてガラス繊維テープに樹脂を含浸させて形成したFRPアブリゲテープを貼着した複合板材に比較し、使用する脆性板材の厚さを半分にまで低減することができる。又、第1及び第2の繊維強化樹脂層102、104の総厚さ(T<sub>1</sub>+T<sub>2</sub>)も、最大0.5~2mm程度とされ、重量の増大をもたらすことはない。

【0017】上記構成の本発明に係る複合板材10は、任意の方法にて製造し得るが、次に説明する製造方法にて製造するのが最も好適である。

【0018】本発明に従った製造方法によると、図2に図示するように、先ず、クロスに織り込まれた強化繊維4からなる支持体シートに、一方向に配列された強化繊維2を接着剤層6'を介して接着して構成される強化繊維シート1が準備される。

【0019】更に説明すると、支持体シート4としては、樹脂浸透性を有するスクリムクロス、ガラスクロス等が使用される。従って、後で詳しくは説明するように、支持体シート4側から、この支持体シート4及び強化繊維2に樹脂、即ち、マトリクス樹脂6の含浸が可能とされる。支持体シート4の厚みとしては、可撓性を有し且つ強化繊維2を支持し得る程度の強度を備えることが必要であり、この観点から、1~500μm、好ましくは5~100μm程度とされる。

【0020】接着剤層6'を形成する接着剤としては、原則として支持体シート4上に強化繊維2を少なくとも一時的に接着できるものならば何でもよいが、マトリクス樹脂6による強化繊維の補強効果と同様な効果を接着剤層にも与えるようにすれば好ましい。その観点から接着剤6'はマトリクス樹脂6との相溶性のよい樹脂を使用することが好ましく、例えばマトリクス樹脂6としてエポキシ樹脂を使用するときには、エポキシ系の接着剤

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を用いることがよい。接着剤層6'の厚みとしては、強化繊維2を一時的に支持体シート4上に接着できればよいことから、5~100 $\mu$ m、好ましくは10~30 $\mu$ m程度あればよい。

【0021】強化繊維2は、これをフィラメントとして収束剤で多数本収束した繊維束または軽度に撚りをかけて収束した繊維束を接着剤層6'上に並べて上方から押し潰すことにより軽度にバラされ、これにより強化繊維2は収束剤または撚りによる結合により複数層に積層した状態で、支持体シート4上に接着剤層6'を介して一方向に配列して接着され、かくして所望の強化繊維シート1が得られる。

【0022】この場合、強化繊維2は、図3(a)に示すように、繊維束2'を接着剤層6'を介して支持体シート4上に密に一方に並べて、繊維束2'を上から押し潰すことにより繊維束2'の下部を接着剤層6'に接着して、図3(b)に示すように、支持体シート2上に横方向に間隔を置かず密に設けてもよく、或いは、図4(a)に示すように、繊維束2'を接着剤層6'介して支持体シート4上に横方向に間隔を開けて一方に並べて、同様に繊維束2'を上から押し潰すことにより繊維束2'の下部を接着剤層6'に接着して、図4(b)に示すように、支持体シート4上に横方向に間隔を置いて疎に設けてもよい。

【0023】繊維束2'は、繊維同士の間、即ちフィラメント同士の間の開繊を行ったものでも、行わないものでもどちらでも使用することができる。繊維束2'の押し潰しの程度は、任意に選定することができるが、例えば強化繊維2として炭素繊維を使用した場合には、直径5~15 $\mu$ mの炭素繊維フィラメントを12000本程度収束した炭素繊維束のとき、これを横方向の幅が5mm程度になるように押し潰すことが一例として挙げられる。

【0024】このようにして作製した強化繊維シート1は、図5に示すように、マトリクス樹脂6と同系の樹脂からなるプライマー6"が塗布された脆性板材100の表面或は裏面とされる一側に、該強化繊維シート1の一方向配列強化繊維2が対面するようにして貼り付けられる。脆性板材100の、強化繊維シート1が位置される側面には予めプライマー6"を塗布するのが好ましいが、場合によっては省略することもできる。

【0025】更に、脆性板材100に配置された強化繊維シート1の外側に位置した支持体シート4側からローラ等によりマトリクス樹脂6を塗布し、それによってマトリクス樹脂6が支持体シート4を通して浸透し、更に、マトリクス樹脂6を強化繊維2にまで含浸させる。次いで、適当な手段にて、樹脂が含浸された強化繊維シート1を脆性板材100へと押圧した状態に維持し、必要に応じて加熱することにより、マトリクス樹脂6を硬化する。

【0026】これにより、図1に示すような、脆性板材100の一側に、一方向に配列された強化繊維2に樹脂6が含浸された第1の繊維強化樹脂層102と、クロスに織り込まれた強化繊維4に樹脂6が含浸された第2の繊維強化樹脂層104とが積層された複合板材10が形成される。

【0027】上記実施例では、脆性板材100には一枚の強化繊維シート1が積層される場合について説明したが、強化繊維シート1は、必要に応じて複数枚積層することができる。この時、積層される強化繊維シート1は、一方向配列強化繊維2の方向が互いに異なる方向に位置するように、互い違いに積層することができる。又、強化繊維シート1は、一方向配列強化繊維2の側が脆性板材100の側に来るようにして貼り付け、積層したが、支持体シート4側が脆性板材100の側となるように貼り付け、積層してもよい。

【0028】更には、他の実施例として、先ず、ローラ、刷毛、吹付け等の適宜な塗布手段により強化繊維シート1上の一方向配列強化繊維2或は支持体シート4にマトリクス樹脂6を塗布して含浸させ、その後、必要に応じてプライマーが塗布された脆性板材の面に、この樹脂が塗布された側が来るようにして強化繊維シート1を1枚或は所望枚数だけ貼り付け、積層し、次いで、強化繊維シート1の外側面にハンドローラ等でマトリクス樹脂を塗布し、そして含浸操作を行うことも可能である。

【0029】本発明にて、マトリクス樹脂としては、硬化剤の配合を調節して室温で硬化するようにしたエポキシ樹脂等とされる室温硬化型樹脂を使用すれば、加熱手段などの必要がなくなり、簡便である。

【0030】上記説明した複合板材10の製造方法によると、プリプレグを積層して複合板材を製造する場合に比して、脆性板材100に対する押圧力、更には、硬化のための加熱手段が簡易なものとなることができるという、製造上の利益がある。又、脆性板材100が湾曲形状とされる場合においても、マトリクス樹脂6を含浸していない状態で強化繊維シート1をこの湾曲面に沿って配置することができるので、作業性が良く且つ正確に配置し得るという利益がある。

【0031】次に、本発明の複合板材10を実施例について更に具体的に説明する。

【0032】実施例1

脆性板材100として、縦×横=600×600mm、厚さ4mmのセラミック板を使用し、強化繊維シート1は次のようにして作製した。

【0033】支持体シート4としては、厚さ30 $\mu$ mとされるガラスクロス(商品名:KS-1020、カネボウ株式会社製)を使用し、この上にエポキシ樹脂を接着剤層6'として20g/m<sup>2</sup>だけ塗布した。

【0034】強化繊維2としては、繊維径が7.0 $\mu$ mとされるPAN系の炭素繊維(東レ株式会社製:商品名



「T-300」)であって、この炭素繊維を12000本収束した炭素繊維束2'を使用した。この炭素繊維束2'を上記支持体シート4の上に、4.6mm間隔にて配列し、上から各繊維束2'の横方向の幅が5mm程度になるように押し潰し、支持体シート4の上に一様に炭素繊維2を配列した。

【0035】前記脆性板材100の一侧にプライマー6"を塗布し、この面に、強化繊維シート1の炭素繊維2が対面するようにして前記強化繊維シート1を貼り付け、更に、支持体シート4側にローラによりマトリクス樹脂6を塗布し、強化繊維2にまで含浸させた。マトリクス樹脂6としては、室温硬化型エポキシ樹脂(商品名:FRレジン(FR-E3)、東燃株式会社製)を使用した。

【0036】この状態で一昼夜放置して、マトリクス樹脂6を硬化した。このようにして作製した複合板材100の、第1及び第2の繊維強化樹脂層102、104における強化繊維及びマトリクス樹脂の配合割合は、重量%で、第1の繊維強化樹脂層102では、強化繊維:マトリクス樹脂=40:60であり、第2の繊維強化樹脂層104では、強化繊維:マトリクス樹脂=30:70であった。又、各繊維強化複合樹脂層102、104の厚さは、第1の繊維強化樹脂層102は、 $T_1=320\mu\text{m}$ 、第2の繊維強化樹脂層104は、 $T_2=60\mu\text{m}$ であった。

【0037】この複合板材10に対して曲げ試験を行なったところ、厚さ4mmのセラミック板100自体の曲げ強度( $0.36\text{kgf/mm}^2$ )の6.7倍の曲げ強度( $2.4\text{kgf/mm}^2$ )を有していた。又、衝撃試験においても、セラミック板100は破壊したが、本実施例の複合板材10は破壊しなかった。

【0038】なお、本実施例にて、曲げ試験は、複合板材10を、長手方向に一方配列強化繊維2が整列するようにして、 $20\times 150\text{mm}$ に切り出して試験片とし、この試験片を距離100mm離間して配置された半径2mmの支持棒の上に配置し、この試験片の中央部に半径5mmのヘッドを、厚さ3.5mmのテフロン板を介して押し当て、ヘッドスピード $2\text{mm/min}$ にて押圧して行なった。

【0039】又、衝撃試験は、 $600\times 600\text{mm}$ の複合板材10を、一方配列強化繊維2の長手方向に沿って距離100mm離間して配置された半径2mmの支持棒の上に配置し、この試験片の中央部に、300mmの高さから重さ500gの鋼球を落下させて行なった。

【0040】比較例1

実施例1と同じセラミック板100の片面に、実施例1にて使用したガラスクロスを貼り付け、実施例1と同じ室温硬化型エポキシ樹脂を含浸させて複合板材を作製した。この状態で一昼夜放置して、マトリクス樹脂を硬化した。

【0041】このようにして作製した複合板材の繊維強化樹脂層における、強化繊維クロス及びマトリクス樹脂の配合割合は、重量%で、強化繊維:マトリクス樹脂=40:60であり、又、繊維強化複合樹脂層の厚さは $320\mu\text{m}$ であった。

【0042】この複合板材に対して実施例1と同じ方法にて曲げ試験及び衝撃試験を行なった。この複合板材は、衝撃試験では破壊しなかったが、曲げ強度は、セラミック板自体の曲げ強度( $0.36\text{kgf/mm}^2$ )の2.8倍の曲げ強度( $1.0\text{kgf/mm}^2$ )しか有しておらず、実施例1に比較し、補強効果が低かった。

【0043】比較例2

実施例1と同じセラミック板100の片面に、実施例1にて使用した炭素繊維束を、4.6mm間隔にて配列し、上から各繊維束の横方向の幅が5mm程度になるように押し潰し、一様に配列した。次いで、実施例1と同じ室温硬化型エポキシ樹脂を炭素繊維に含浸させて複合板材を作製した。この状態で一昼夜放置して、マトリクス樹脂を硬化した。

【0044】このようにして作製した複合板材の繊維強化樹脂層における、強化繊維とマトリクス樹脂の配合割合は、重量%で、強化繊維:マトリクス樹脂=40:60であり、又、繊維強化複合樹脂層の厚さは $320\mu\text{m}$ であった。

【0045】この複合板材に対して実施例1と同じ方法にて曲げ試験及び衝撃試験を行なった。この複合板材は、曲げ強度は、セラミック板自体の曲げ強度( $0.36\text{kgf/mm}^2$ )の6.9倍の曲げ強度( $2.5\text{kgf/mm}^2$ )を有していたが、衝撃試験においては、破壊してしまい、十分な補強効果を達成し得なかった。

【0046】

【発明の効果】以上の如くに構成される本発明に係る複合板材は、例えば脆性板材の厚さを5mm以下とした場合においても、十分な耐衝撃性及び曲げ強度を発揮することができ、取扱い性の向上及び重量の軽減を図ることができる。又、本発明に従った複合板材の製造方法によれば、押圧手段及び加熱手段などを簡易なものとして行うことができ、しかも、例えば脆性板材が湾曲した形状であったとしても問題なく、極めて好適に製造することができる。

【図面の簡単な説明】

【図1】本発明に係る複合板材の一実施例の断面構成図である。

【図2】本発明の複合板材を製造するのに使用される強化繊維シートの断面構成図である。

【図3】強化繊維シートの製造法を説明する断面構成図である。

【図4】強化繊維シートの製造法を説明する断面構成図である。

【図5】本発明の複合板材の製造方法の一実施例を説明

する断面構成図である。

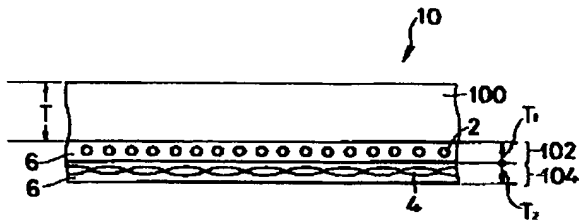
【符号の説明】

- 1 強化繊維シート  
2 一方向配列強化繊維  
4 強化繊維クロス（支持体シート）  
6 マトリクス樹脂

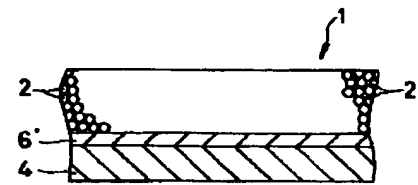
- 6' 接着剤層  
6'' プライマー  
100 脆性板材  
102 第1繊維強化樹脂層  
104 第2繊維強化樹脂層

- 接着剤層  
プライマー  
脆性板材  
第1繊維強化樹脂層  
第2繊維強化樹脂層

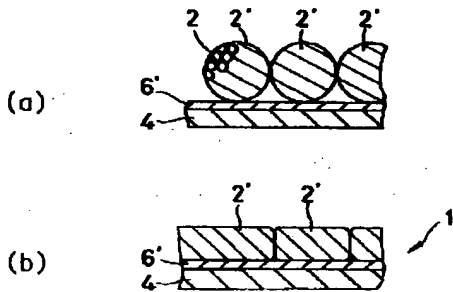
【図1】



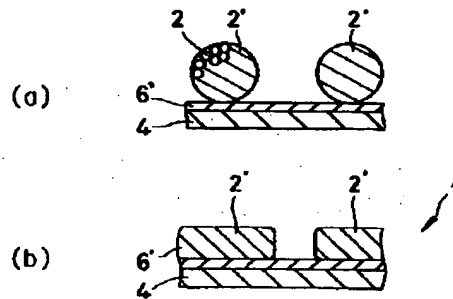
【図2】



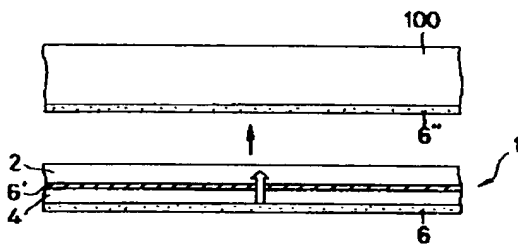
【図3】



【図4】



【図5】



PTO 2001-3231

CY=JP DATE=19940308 KIND=A  
PN=06064076

COMPOSITE BOARD AND MANUFACTURE THEREOF  
[Fukugo itazai oyobi sono seizo hoho]

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UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. July 2001

Translated by: Diplomatic Language Services, Inc.

PUBLICATION COUNTRY	(19) : JP
DOCUMENT NUMBER	(11) : 06064076
DOCUMENT KIND	(12) : A (13) :
PUBLICATION DATE	(43) : 19940308
PUBLICATION DATE	(45) :
APPLICATION NUMBER	(21) : 04244164
APPLICATION DATE	(22) : 19920830
ADDITION TO	(61) :
INTERNATIONAL CLASSIFICATION	(51) : B32B 5/00; B32B 17/04; B32B 19/00; B44C 3/02
DOMESTIC CLASSIFICATION	(52) :
PRIORITY COUNTRY	(33) :
PRIORITY NUMBER	(31) :
PRIORITY DATE	(32) :
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TITLE	(54) : COMPOSITE BOARD AND MANUFACTURE THEREOF
FOREIGN TITLE	[54A] : FUKUGO ITAZAI OYOBI SONO SEIZO HOHO

(Claims)

(Claim 1) Composite board so characterized that at least a first fiber-reinforced resin layer having resin impregnated into reinforced fiber arrayed in one direction and a second fiber-reinforced resin layer having resin impregnated into reinforced fiber woven into cloth are laminated onto one side of a plate-shaped brittle substrate.

(Claim 2) Manufacture of composite board so characterized that (a) a plate-shaped brittle substrate is prepared, (b) a reinforced fiber sheet is prepared that is comprised by adhering reinforced fiber arrayed in one direction to a support sheet comprised of reinforced fiber woven into cloth by way of an adhesive layer, (c) the above-mentioned reinforced fiber sheet is positioned on one side of the above-mentioned brittle substrate, and (d) a matrix resin is coated onto the outer side of the above-mentioned reinforced fiber sheet, and matrix resin is impregnated into the above-mentioned support sheet and the above-mentioned reinforced fiber and cured.

(Claim 3) Manufacture of composite board so characterized that (a) a plate-shaped brittle substrate is prepared, (b) a reinforced fiber sheet is prepared that is comprised by adhering reinforced fiber arrayed in one direction to a support sheet comprised of reinforced fiber woven into cloth by way of an adhesive layer, (c) a matrix resin is coated onto one side of the above-mentioned reinforced fiber sheet, then the above-mentioned reinforced fiber sheet is pasted to the above-mentioned brittle substrate with this side against one side of the above-mentioned brittle substrate, and (d) a matrix resin is coated onto the outer side of the above-mentioned reinforced fiber sheet, and matrix resin is

impregnated into the above-mentioned support sheet and the above-mentioned reinforced fiber and cured.

(Detailed Description of the Invention)

(Industrial Field of Application) This invention pertains to a composite board that has fiber-reinforced resin layers pasted onto the front or back side of a brittle board such as a ceramic board, marble or other natural rock thin plate, tile, or a thin concrete slab, has great shock resistance and bending strength, has thin board thickness and can be made lighter in weight, and can be used ideally for applications such as interior or exterior construction paneling, floors, table tops, or doors.

(Prior Art) In recent years, materials such as ceramic boards, marble or other natural rock thin plates, tile, or thin concrete slabs have come to be used for applications such as interior or exterior construction paneling, floors, table tops, or doors. These materials, however, have high specific gravity and are expensive. Therefore, to decrease weight and improve handling, as well as to reduce material cost, transport cost, or processing cost, it is desirable that their thickness be as thin as possible. Making these materials thin, however, produces the problems that they become brittle, have reduced shock resistance, and require considerable care in handling.

To solve such problems, Japan Kokai Patent No. 63-222850 offers a composite board in which FRP prepreg tape formed by impregnating resin into fiberglass tape is pasted as a reinforcing fiber onto one side of a brittle board of this type that is about 10 mm thick.

(Problems that the Invention is to Solve) However, according to

research results by the present inventors, it was discovered that the brittle board in the composite board constructed in this way disclosed by this patent must be at least about 10 mm thick to obtain adequate shock resistance. For example, when the brittle board is less than 5 mm thick, not only is it unable to obtain adequate shock resistance, it also has markedly reduced bending strength.

Therefore, the purpose of this invention is to offer a composite board and manufacture thereof that can achieve adequate shock resistance and bending strength, improved handling, and reduced weight even using a brittle board that is, for example, less than 5 mm thick.

(Means of Solving the Problems) The purpose given above is realized by the composite board and manufacture thereof with which this invention is concerned. Stated briefly, this invention is a composite board so characterized that at least a first fiber-reinforced resin layer having resin impregnated into reinforced fiber arrayed in one direction and a second fiber-reinforced resin layer having resin impregnated into reinforced fiber woven into cloth are laminated onto one side of a plate-shaped brittle substrate.

Such a composite board can be manufactured ideally by manufacture so characterized that (a) a plate-shaped brittle substrate is prepared, (b) a reinforced fiber sheet is prepared that is comprised by adhering reinforced fiber arrayed in one direction to a support sheet comprised of reinforced fiber woven into cloth by way of an adhesive layer, (c) the above-mentioned reinforced fiber sheet is positioned on one side of the above-mentioned brittle substrate, and (d) a matrix resin is coated onto the outer side of the above-mentioned reinforced fiber sheet, and

matrix resin is impregnated into the above-mentioned support sheet and the above-mentioned reinforced fiber and cured.

As another method, the composite board of this invention can be manufactured ideally by manufacture so characterized that (a) a plate-shaped brittle substrate is prepared, (b) a reinforced fiber sheet is prepared that is comprised by adhering reinforced fiber arrayed in one direction to a support sheet comprised of reinforced fiber woven into cloth by way of an adhesive layer, (c) a matrix resin is coated onto one side of the above-mentioned reinforced fiber sheet, then the above-mentioned reinforced fiber sheet is pasted to the above-mentioned brittle substrate with this side against one side of the above-mentioned brittle substrate, and (d) a matrix resin is coated onto one side of the above-mentioned reinforced fiber sheet, and matrix resin is impregnated into the above-mentioned support sheet and the above-mentioned reinforced fiber and cured.

(Working Examples) Next, the composite board and manufacture thereof of this invention are explained in greater detail conforming to the figures.

As shown, for example, in Figure 1, composite board (10) of this invention has first fiber-reinforced resin layer (102) and second fiber-reinforced resin layer (104) laminated onto the front or back side of a plate-shaped brittle substrate, namely brittle board (100), such as ceramic board, marble or other natural rock thin plate, tile, or thin concrete slab. Thickness (T) of brittle board (100) can be as thin as possible. For example, a board comprised of ceramic or marble can be used that is as thin as about 2 to 4 mm.



In addition, first fiber-reinforced resin layer (102) is formed by impregnating resin (matrix resin) (6) into reinforced fiber arrayed in one direction (2), and second fiber-reinforced resin layer (104) is formed by impregnating resin (matrix resin) (6) into reinforced fiber woven into cloth (fabric) (4).

For reinforced fiber (2) used in the above-mentioned first fiber-reinforced resin layer (102), carbon fiber is most preferred, but for example, one type selected from inorganic fibers such as boron fiber, glass fiber, alumina fiber, silicon carbide fiber, or silicon nitride fiber; organic fibers such as alumide fiber, polyallylate fiber, polyethylene fiber, or polyester fiber; or metallic fibers such as titanium fiber, amorphous fiber, or stainless steel fiber can also be used. Alternately, a hybrid mode comprised of several types can be used. In addition, cloth reinforced fiber (4) used in the above-mentioned second fiber-reinforced resin layer (104) is preferably an organic fiber such as alumide fiber, polyallylate fiber, polyethylene fiber, or polyester fiber made into cloth.

Normally, the same resin is used for matrix resin (6) impregnated into reinforced fibers (2) and (4) used in first and second fiber-reinforced resin layers (102) and (104). For example, a thermosetting matrix resin such as epoxy resin, unsaturated polyester resin, polyurethane resin, diallyl phthalate resin, or phenolic resin can be used. Furthermore, an appropriate amount of curing agent and other additives such as imparting agents are added such that this can cure at a curing temperature of 50 to 200°C, and preferably room temperature.

To cite preferred examples, this matrix resin is preferably an

epoxy resin. Examples of epoxy resins that can be used are one type or several types selected from (1) glycidyl ether epoxy resins (Bisphenol A, F, and S epoxy resins, Novolak epoxy resins, brominated Bisphenol A epoxy resins); (2) cyclic aliphatic epoxy resins; (3) glycidyl ester epoxy resins; (4) glycidyl amine epoxy resins such tetraglycidyl diaminodiphenylmethane or triglycidyl-p-aminophenol; (5) heterocyclic epoxy resins; and other epoxy resins. Bisphenol A, F, and S glycidyl amine epoxy resins are especially ideal. For the curing agent, curing agents such as dicyandiamide (DICY), diaminodiphenylsulfone (DDS), diaminodiphenylmethane (DDM), and acid anhydrides such as hexahydrophthalic anhydride (HHPA) or methylhexahydrophthalic anhydride (MHHPA) are used, but amine curing agents are especially ideal.

The content ratio of matrix resin (6) impregnated into reinforced fibers (2) and (4) used in first and second fiber-reinforced resin layers (102) and (104) can be adjusted as desired, but normally is a ratio of 20 to 70 wt% reinforced fiber to 80 to 30 wt% matrix resin. In addition, thickness ( $T_1$ ) and ( $T_2$ ) of each of fiber-reinforced resin layers (102) and (104) can be as thin as close to the diameter of the reinforced fiber used, but normally is about 50 to 1000  $\mu\text{m}$ .

Because composite board (10) constructed in this way with which this invention is concerned has first fiber-reinforced resin layer (102) having reinforced fiber arrayed in one direction (2) and second fiber-reinforced resin layer (104) having reinforced fiber cloth (4) laminated onto brittle board (100), it has markedly improved shock resistance and bending strength. As a result, the thickness of the brittle board used can be reduced to half or less compared to a composite board in which

FRP prepreg tape formed by impregnating resin into fiberglass tape is pasted as a reinforcing fiber onto one side of a brittle board that is about 10 mm thick as described in Japan Kokai Patent No. 63-222850 cited above. In addition, thickness ( $T_1 + T_2$ ) of first and second fiber-reinforced resin layers (102) and (104) is a maximum of about 0.5 to 2 mm, and does not lead to increased weight.

Although composite board (10) constructed as described above with which this invention is concerned can be manufactured by any method desired, ideally, it is manufactured by the methods explained below:

According to manufacturing following this invention, as shown in Figure 2, first, reinforced fiber sheet (1) is prepared that is comprised by adhering reinforced fiber arrayed in one direction (2) to a support sheet comprised of reinforced fiber woven into cloth (4) by way of adhesive layer (6').

To explain this further, a resin-permeable cloth such as screen cloth or glass cloth is used as support sheet (4). Therefore, as explained in detail below, resin, namely matrix resin (6), can impregnate into this support sheet (4) and reinforced fiber (2) from the support sheet (4) side. Support sheet (4) must be thick enough to allow flexibility and still have enough strength to support reinforced fiber (2). From this standpoint, this thickness is 1 to 500  $\mu\text{m}$ , and preferably about 5 to 100  $\mu\text{m}$ .

For the adhesive that forms adhesive layer (6'), as a rule, any adhesive can be used so long as it can adhere reinforced fiber (2) onto support sheet (4) at least temporarily, but preferably, this adhesive has a comparable effect on the adhesive layer to the reinforcing effect

produced by matrix resin (6). From this standpoint, an adhesive that has good miscibility with matrix resin (6) is used for adhesive layer (6'). For example, when an epoxy resin is used for matrix resin (6), an epoxy adhesive may be used. Because adhesive layer (6') need only be thick enough to adhere reinforced fiber (2) onto support sheet (4) temporarily, this thickness may be 5 to 100  $\mu\text{m}$ , and preferably about 10 to 30  $\mu\text{m}$ .

Using reinforced fiber (2) as filaments, many fiber bundles bundled by a bundling agent or many fiber bundles bundled by twisting are aligned on top of adhesive layer (6') and lightly loosened by squashing from above. As a result, having been stacked in several layers and bonded by a bundling agent or twisting, reinforced fiber (2) is adhered arrayed in one direction onto support sheet (4) by way of adhesive layer (6'), and the desired reinforced fiber sheet (1) is thus obtained.

During this process, fiber bundles (2') may be densely aligned in one direction on top of support sheet (4) by way of adhesive layer (6') as shown in Figure 3(a) and the lower part of fiber bundles (2') adhered to adhesive layer (6') by squashing fiber bundles (2') from above such that reinforced fiber (2) is installed horizontally and densely without gaps on top of support sheet (2) as shown in Figure 3(b), or fiber bundles (2') may be aligned horizontally in one direction with gaps on top of support sheet (4) by way of adhesive layer (6') as shown in Figure 4(a) and the lower part of fiber bundles (2') adhered to adhesive layer (6') by squashing fiber bundles (2') from above in the same way such that reinforced fiber (2) is installed horizontally and sparsely leaving gaps on top of support sheet (2) as shown in Figure 4(b).

Fiber bundles (2') can be used either opened or not opened between fibers; that is, between filaments. The degree of squashing of fiber bundles (2') can be set as desired, but when carbon fiber is used as reinforced fiber (2), for example, using carbon fiber bundles comprised by bundling about 12,000 carbon fiber filaments measuring 5 to 15  $\mu\text{m}$  in diameter, the example may be cited of squashing this such that it measures about 5 mm in horizontal width.

As shown in Figure 5, reinforced fiber sheet (1) fabricated in this way is pasted such that reinforced fiber arrayed in one direction (2) of said reinforced fiber sheet (1) faces the side taken as the front or back side of brittle board (100) that is coated with primer (6'') comprised of the same type of resin as matrix resin (6). Preferably, primer (6'') is coated ahead of time onto the side of brittle board (100) on which reinforced fiber sheet (1) is positioned, but in some cases, this can be omitted.

Furthermore, matrix resin (6) is coated from the support sheet (4) side by a means such a roller onto the outer side of reinforced fiber sheet (1) positioned on brittle board (100). As a result, matrix resin (6) permeates through support sheet (4), and impregnates as far as reinforced fiber (2). Next, reinforced fiber sheet (1) impregnated with resin is held compressed against brittle board (100) by an appropriate means, and matrix resin (6) is cured by heating as required.

As a result, composite board (10) is formed that has first fiber-reinforced resin layer (102) having resin (6) impregnated into reinforced fiber arrayed in one direction (2) and second fiber-reinforced resin layer (104) having resin (6) impregnated into

reinforced fiber woven into cloth (4) laminated onto one side of brittle board (100) as shown in Figure 1.

The working example described above was explained for the case of one reinforced fiber sheet (1) laminated to brittle board (100), but several reinforced fiber sheets (1) can be laminated together as required. In this case, the reinforced fiber sheets (1) laminated can be laminated in different directions such that reinforced fiber arrayed in one direction (2) is positioned in different directions. In addition, reinforced fiber sheet (1) was pasted and laminated such that the side with reinforced fiber arrayed in one direction (2) was against brittle board (100), but this also may be pasted and laminated such that the side with support sheet (4) is against brittle board (100).

Furthermore, as another working example, first, matrix resin (6) is coated by an appropriate coating means such as roller, brush, or spraying and impregnated into reinforced fiber arrayed in one direction (2) or support sheet (4) on top of reinforced fiber sheet (1). Next, one sheet or the number of sheets desired of reinforced fiber sheet (1) is pasted and laminated onto one side of a brittle board that has been coated as required with a primer, then a matrix resin is coated by a means such as a hand-roller onto the outer side of reinforced fiber sheet(s) (1), and the same impregnation operation is performed.

When a room-temperature-curing resin such as an epoxy resin that is adjusted in content of curing agent so as to cure at room temperature is used as the matrix resin in this invention, there is no need for a heating means or the like, and manufacture is simplified.

According to the manufacture of composite board (10) explained

above, this method obtains the advantage in terms of manufacture that both the pressing force against brittle board (100) and the heating means for curing can be simplified compared to when a composite board is manufactured by laminating a prepreg. In addition, even when brittle board (100) is curved, because reinforced fiber sheet (1) can be positioned along this curved surface before impregnating with matrix resin (6), this method obtains the advantage that ease of operation is improved and the sheet can be positioned accurately.

Next, composite board (10) of this invention is explained concretely by working examples.

#### Working Example 1

A ceramic board measuring 600 x 600 mm height x width and 4 mm in thickness was used as brittle board (100), and reinforced fiber sheet (1) was fabricated as follows:

30  $\mu$ m thick glass cloth (trade name: KS-1020, manufactured by Kanebo, Ltd.) was used for support sheet (4), and epoxy resin was coated on top of this as adhesive layer (6') at a ratio of exactly 20 g/m<sup>2</sup>.

7.0  $\mu$ m diameter PAN-type carbon fiber (trade name: "T-300," manufactured by Toray Industries) was used for reinforced fiber (2), and 12,000 of these carbon fibers were bundled to form carbon fiber bundle (2'). These carbon fiber bundles (2') were arrayed on top of the above-mentioned support sheet (4) at a spacing of 4.6 mm, carbon fiber bundles (2') were squashed from above such that they measured about 5 mm in horizontal width, and carbon fiber (2) was evenly arrayed on top of support sheet (4).

Primer (6'') was coated onto one side of the above-mentioned brittle

board (100), and the above-mentioned reinforced fiber sheet (1) was pasted such that carbon fiber (2) faced this side. Furthermore, matrix resin (6) was coated by a roller onto the support sheet (4) side, and impregnated as far as carbon fiber (2). A room-temperature-curing type epoxy resin (trade name: FR resin (FR-E3), manufactured by Tonen Co., Ltd.) was used for matrix resin (6).

Matrix resin (6) was cured by leaving in this state overnight. The content ratio of reinforced fiber to matrix resin in first and second fiber-reinforced resin layers (102) and (104) of composite board (10) fabricated in this way was reinforced fiber to matrix resin = 40:60 wt% in first fiber-reinforced resin layer (102), and reinforced fiber to matrix resin = 30:70 wt% in second fiber-reinforced resin layer (104). The thickness of first and second fiber-reinforced resin layers (102) and (104) was first fiber-reinforced resin layer (102):  $T_1 = 320 \mu\text{m}$ , and second fiber-reinforced resin layer (104):  $T_2 = 60 \mu\text{m}$ .

When a bending test was conducted on this composite board (10), it had bending strength ( $2.4 \text{ kgf/mm}^2$ ) that was 6.7 times the bending strength ( $0.36 \text{ kgf/mm}^2$ ) of 4 mm thick ceramic board (100) by itself. In addition, in an impact test, ceramic board (100) broke, but composite board (10) of this working example did not break.

Moreover, the bending test in this working example was conducted by cutting composite board (10) into a 20 x 150 mm sample piece such that reinforced fiber arrayed in one direction (2) was aligned lengthwise, placing this sample piece on 2 mm diameter support bars spaced every 100 mm, then pressing a 5 mm diameter head against the center of the sample piece by way of a 3.5 mm diameter Teflon plate, and compressing at a



head speed of 2 mm/min.

The impact test was conducted by placing 600 x 600 mm composite board (10) on 2 mm diameter support bars spaced every 100 mm lengthwise along reinforced fiber arrayed in one direction (2), and dropping a steel ball weighing 500 g from a height of 300 mm onto the center of this test piece.

#### Comparative Example 1

A composite board was fabricated by pasting the glass cloth used in Working Example 1 onto one side of the same ceramic board (100) as in Working Example 1 and impregnating with the same room-temperature-curing type epoxy resin as in Working Example 1. Matrix resin (6) was cured by leaving in this state overnight.

The content ratio of reinforced fiber to matrix resin in the fiber-reinforced resin layer of the composite board fabricated in this way was reinforced fiber to matrix resin = 40:60 wt%. The thickness of the fiber-reinforced resin layer was 320  $\mu\text{m}$ .

A bending test and impact test were conducted on this composite board by the same method as in Working Example 1. As a result, this composite board had bending strength ( $1.0 \text{ kgf/mm}^2$ ) that was only 2.8 times the bending strength ( $0.36 \text{ kgf/mm}^2$ ) of the ceramic board by itself, and had low reinforcing effect compared to the working example.

#### Comparative Example 2

The carbon fiber bundles used in Working Example 1 were arrayed on one side of the same ceramic board (100) as in Working Example 1 at a spacing of 4.6 mm, and the carbon fiber bundles were squashed from above such that they measured about 5 mm in horizontal width and were evenly

arrayed. Next, a composite board was fabricated by impregnating the same room-temperature-curing type epoxy resin as in Working Example 1 into the carbon fiber. Matrix resin (6) was cured by leaving in this state overnight.

The content ratio of reinforced fiber to matrix resin in the fiber-reinforced resin layer of the composite board fabricated in this way was reinforced fiber to matrix resin = 40:60 wt%. The thickness of the fiber-reinforced resin layer was 320  $\mu\text{m}$ .

A bending test and impact test were conducted on this composite board by the same method as in Working Example 1. As a result, this composite board had bending strength ( $2.5 \text{ kgf/mm}^2$ ) that was 6.9 times the bending strength ( $0.36 \text{ kgf/mm}^2$ ) of the ceramic board by itself, but it broke in the impact test, and so did not achieve an adequate reinforcing effect.

(Effects of the Invention) The composite board constructed as described above with which this invention is concerned can achieve adequate shock resistance and bending strength, improved handling, and reduced weight even using a brittle board that is, for example, less than 5 mm thick. In addition, according to the manufacture of a composite board following this invention, the pressing means and heating means can be simplified. Moreover, there are no problems even when the brittle board is curved, for example, and a composite board can be manufactured under extremely ideal conditions.

(Brief Explanation of the Figures)

Figure 1 is a schematic section of one working example of the composite board with which this invention is concerned.

Figure 2 is a schematic section of a reinforced fiber sheet used to manufacture a composite board of this invention.

Figure 3 is a schematic section that illustrates manufacture of a reinforced fiber sheet.

Figure 4 is a schematic section that illustrates manufacture of a reinforced fiber sheet.

Figure 5 is a schematic section that illustrates one working example of manufacture of a composite board of this invention.

(Key to Part Numbers)

- 1 reinforced fiber sheet
- 2 reinforced fiber arrayed in one direction
- 4 reinforced fiber cloth (support sheet)
- 6 matrix resin
- 6' adhesive layer
- 6" primer
- 100 brittle board
- 102 first fiber-reinforced resin layer
- 104 second fiber-reinforced resin layer

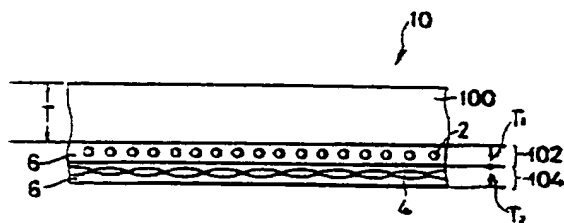


Figure 1

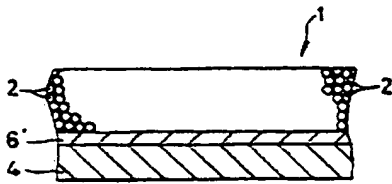


Figure 2

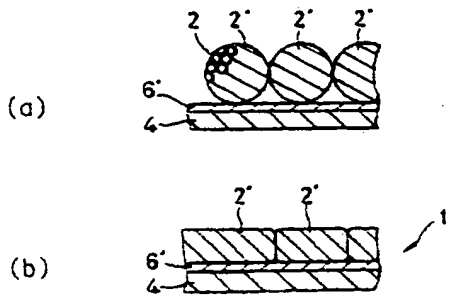


Figure 3

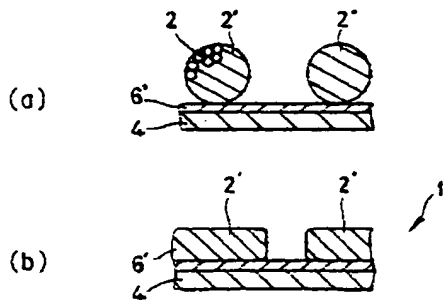


Figure 4

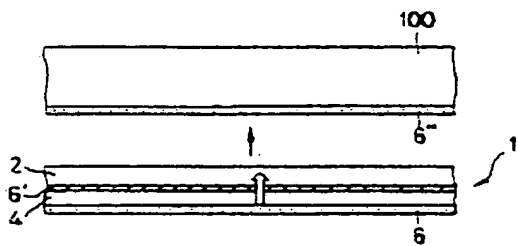


Figure 5

## JAPANESE PATENT OFFICE (JP)

(12) OFFICIAL PATENT DISCLOSURE BULLETIN (A)

(11) APPL. DISCL. N.: 0664076

(43) APPLICATION DISCLOSED ON: 8<sup>th</sup> MARCH 1994

(51) Intern'l. Cl.	Id. Internal Protocol FI
B32B 5/00	A 7016-4F
17/04	Z
19/00	
B44C 3/02	A 3134-3K
EXAM: NOT REQUIRED	NUMBER OF CLAIMS: 3 (TOTAL 6 PAGES)
(21) APPLICATION N.: 04244164	(71) APPLICANT:
(22) FILING DATE: 20 <sup>th</sup> August 1992	Id. N. 390022998
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(54) [TITLE OF THE INVENTION]

COMPOSITE PLATE MATERIAL AND ITS MANUFACTURE

(57) [ABSTRACT]

[PURPOSE] To provide a composite plate material and a manufacture therefor which can display a sufficient shock resistance and bending strength even when the thickness of a fragile plate material is not larger than 5 mm, and improve the handling convenience and reduce the weight.

[CONSTITUTION] A first fiber-reinforced resin layer 102 and a second fiber-reinforced resin layer 104 are laminated on the front or rear surface of a fragile plate material 100

such as a ceramic plate material, a thin sheet of natural stone such as marble, a tile or concrete thin sheet, etc. The first fiber-reinforced resin layer 102 is formed by impregnating with a resin (matrix resin) 6 reinforcing fibers 2 orientated in one direction, while the second fiber-reinforced resin layer 104 is formed by impregnating with the resin (matrix resin) 6 reinforcing fibers 4 interwoven into a cloth (fabric).

[CLAIMS]

[CLAIM 1] A composite plate material characterised in that it is formed by laminating a first fiber-reinforced resin layer, wherein the reinforcing fibers are impregnated with a resin, and are arranged in at least one direction onto a side of a fragile plate-shaped base, and a second fiber-reinforced resin layer, wherein the reinforcing fibers are interwoven into a cloth (fabric), and impregnated with a resin.

[CLAIM 2] A manufacturing method of a composite plate material, characterised in that: (a) a fragile plate-shaped base is prepared; (b) a reinforcing fiber sheet is formed, by adhering, by means of an adhesive layer, reinforcing fibers orientated in one direction onto a supporting sheet, made of reinforcing fibers interwoven into a cloth; (c) said reinforcing fiber sheet is positioned onto a side of said fragile base plate; (d) a resin matrix is applied onto the outer surface of said reinforcing fiber sheet, and said

supporting and reinforcing fiber sheets are subsequently impregnated with the resin matrix and hardened.

[CLAIM 3] A manufacturing method of a composite plate material characterised in that: (a) a fragile plate-shaped base is prepared; (b) a reinforcing fiber sheet is formed by adhering, by means of an adhesive layer, reinforcing fibers orientated in one direction onto a supporting sheet, composed of reinforcing fibers interwoven into a cloth; (c) after the matrix resin has been positioned onto a side of said fragile base plate, said reinforcing fiber sheet is adhered onto said base plate by facing the former to a side of said fragile base plate surface; (d) a resin matrix is applied onto the outer surface of said reinforcing fiber sheet, and said supporting and reinforcing fiber sheets are subsequently impregnated with the resin matrix and hardened.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[FIELD OF THE INVENTION] The present invention relates to a composite plate material, wherein a fiber-reinforced resin layer is adhered onto the front or the rear surface of a fragile plate material such as a ceramic plate material, a thin sheet of natural stone such as marble, a tile or concrete thin sheet, etc., having a remarkable shock resistance and bending strength. Moreover, since the plate material can be very thick, the weight thereof can be



further reduced, thus being suitable for interior and exterior trims of buildings, floorings, table top boards, doors, etc.

[0002]

[PRIOR ART] In recent years, ceramic plate materials, thin sheets of natural stone such as marble, tiles or concrete thin sheets, etc. have been utilised as interior and exterior trims of buildings, flooring, table top boards, doors, etc., however such materials have a high specific weight, and furthermore are expensive. Hence, the attainment of a minimum material thickness is desirable in order to reduce the weight and to improve the handling convenience thereof, concurrently cutting the material costs, as well as the transport and working costs thereof. However, reducing the thickness of the material entails a decrease in the shock resistance thereof, and the material becomes fragile, thus requiring great care in handling.

[0003] In order to overcome those drawbacks, JP Shô 63-222850 teaches a composite plate material, wherein a FRP pre-impregnated tape, impregnated with a resin using glass fiber as reinforcing fiber, is adhered onto a 10 mm thick side of such fragile plate material.

[0004]

[PROBLEMS TO BE SOLVED BY THE INVENTION] However, tests carried out by the present inventors highlighted that, in order to provide a sufficient shock resistance, the

thickness of a composite plate material having the aforementioned taught structure should be of at least 10 mm; e.g., in case of a fragile plate material wherein the thickness is of less than 5 mm, not only its shock resistance tested insufficient, the bending strength thereof was remarkably reduced as well.

[0005] Therefore, a purpose of the present invention is that of providing a composite plate material and manufacture therefor which can display sufficient shock resistance and bending strength even when the thickness of a fragile plate material is not larger than 5 mm, and improve the handling convenience and reduce the weight.

[0006]

[MEANS TO SOLVE THE PROBLEMS] The abovementioned purpose is attained by means of the composite plate material and of the manufacture thereof according to the present invention. In short, the present invention consists of a composite plate material characterised in that a first fiber-reinforced resin layer formed impregnating with a resin reinforcing fibers arranged in at least one direction, and a second fiber-reinforced resin layer formed impregnating with a resin reinforcing fibers interwoven into a cloth, are laminated onto a side of a plate-shaped fragile base.

[0007] Preferably, such composite plate material can be manufactured according to a manufacturing process characterised in that: (a) a fragile plate-shaped base is

prepared beforehand; (b) a reinforcing fiber sheet formed by adhering, by means of an adhesive layer, reinforcing fibers orientated in one direction onto a supporting sheet, made of reinforcing fibers interwoven into a cloth; (c) said reinforcing fiber sheet is positioned onto a side of said fragile base plate; (d) a resin matrix is applied onto the outer surface of said reinforcing fiber sheet, and said supporting and reinforcing fiber sheets are subsequently impregnated with the resin matrix and hardened.

[0008] Alternatively, said composite plate material can also preferably be manufactured according to a manufacturing process characterised in that: (a) a fragile plate-shaped base is prepared beforehand; (b) a reinforcing fiber sheet is formed, by adhering, by means of an adhesive layer, reinforcing fibers orientated in one direction onto a supporting sheet, composed of reinforcing fibers interwoven into a cloth; (c) after the matrix resin has been positioned onto a side of said fragile base plate, said reinforcing fiber sheet is adhered onto said base plate by facing the former to a side of said fragile base plate surface; (d) a resin matrix is applied onto the outer surface of said reinforcing fiber sheet, and said supporting and reinforcing fiber sheets are subsequently impregnated with the resin matrix and hardened.

[0009]

[DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS]

The composite plate material and its manufacture according to the present invention will hereinafter be described in detail making reference to the annexed drawings.

[0010] The composite plate material 10 according to the present invention is formed laminating a first fiber-reinforced resin layer 102 and a second fiber-reinforced resin layer 104 on the front or rear surface of a fragile plate 100, such as a ceramic plate material, a thin sheet of natural stone such as marble, or a tile or a concrete thin sheet, and the like. The sole limitations of the thickness (T) of the plate material 100 are those inherent to the manufacturing process, e.g., even a 2-4 mm thickness can be utilised in a ceramic or marble plate material.

[0011] Moreover, the first fiber-reinforced resin layer 102 is formed impregnating with the resin (matrix resin) 6 the reinforcing fibers 2 orientated in one direction, and the second fiber-reinforced resin layer 104 is formed impregnating with resin (matrix resin) 6 the reinforcing fibers 4 interwoven into a cloth (fabric).

[0012] Preferably, carbon fibers are adopted as the reinforcing fibers 2 utilised in the abovementioned fiber-reinforced resin layer 102, however inorganic fibers like boron fibers, glass fibers, alumina fibers, silicon carbide fibers, silicon nitride fibers, etc., and organic fibers like aramid fibers, polyarylate fibers, polyethylene

fibers, polyester fibers, or metallic fibers like titanium fibers, amorphous fibers, stainless steel fibers, etc., or hybrid fibers made of a mixture thereof can be utilised as well. Furthermore, in the second fiber-reinforced resin layer 104, preferably carbon fibers, glass fibers, or organic fibers like aramid fibers, polyarylate fibers, polyethylene fibers, polyester fibers can be utilised as reinforcing fibers 4 of the cloth.

[0013] The matrix resin 6 that impregnates the reinforcing fiber 2 and 4 in the first and second fiber-reinforced resin layers 102 and 104 can be a common resin, e.g. thermoset matrix resins like epoxy resins, unsaturated polyethylene resins, polyurethane resins, diarylphthalate resins, phenolic resins, etc., can be utilised. Furthermore, hardening agents or other additives, e.g. additives providing bendability can be added in order to satisfy specific needs in order to obtain a hardening with a temperature preferably comprised in the range 50-200 °C, more preferably with a uniform temperature.

[0014] A preferred embodiment can be realised using an epoxy resin as matrix resin, e.g., among suitable epoxy resins there can be (1) glycidyl ether type epoxy resins (bisphenol A, F, S, type epoxy resins; novolac type epoxy resins; bromate bisphenol A type epoxy resins); (2) epoxy resins belonging to the cyclic fats group; (3) glycidyl ester type epoxy resins; (4) glycidyl amine-type epoxy

resins, tetra-glycidyl amino diphenol methane, tri glycidyl-p-amino phenol epoxy resins, etc.; (5) cyclic epoxy resins made of various elements; one or more epoxy resins selected among the above-mentioned ones can be utilised; in particular, preferably bisphenol A,S,F, glycidyl amine- type epoxy resins are utilised. Moreover, amine-type hardening agents like dicyanamide (DICY), diamino diphenol sulphone (DDS), diamino diphenol methane (DDM), acidic anhydrides like hexa hydro phthalic anhydride (HHPA), methyl hexa hydro phthalic anhydride (MHHPA) can be utilised, however, more preferably hardening agents of the amine group are utilised.

[0015] Moreover, the combination ratio of reinforcing fibers 2 and 4 contained in the first and second fiber-reinforced resin layers 102 and 104 can be set according to the specific needs, however usually the weight percentage is set according to the following proportion:

reinforcing fibers : matrix resins = 20~70 : 80~30;

furthermore, the thicknesses ( $T_1$ ) and ( $T_2$ ) of each fiber-reinforced resin layer 102 and 104 can match the diameter of the reinforcing fibers utilised, however usually it is set within a 50~1000 $\mu$ m range.

[0016] In a composite plate material 10 according to the present invention thus manufactured, both the shock resistance and the bending strength thereof are remarkably

enhanced thanks to the laminating of the first fiber-reinforced resin layer 102, having the reinforcing fibers 2 orientated in one direction, and of the second fiber-reinforced resin layer 104, having the reinforcing fibers cloth 4, onto a fragile plate material 100. Thus, the thickness of the adopted fragile plate material is reduced of more than 50% compared to the aforementioned composite plate material taught in JP Shô 63-222850, wherein a FRP tape, obtained by impregnating a glass fiber (as reinforcing fibers) tape with resin, was adhered to a 10 mm thick surface of a composite plate material. Moreover, a weight increase is avoided since also the total thickness ( $T_1+T_2$ ) of the first and second fiber-reinforced resin layers 102, 104 does not exceed 0.5~2 mm.

[0017] The composite plate material 10 manufactured according to the present invention can be formed according to several manufacturing processes; hereinafter one preferable manufacturing process thereof is disclosed.

[0018] According to the manufacture in accordance with the present invention, firstly, as shown in Fig. 2, a reinforcing fiber sheet 1, formed by adhering with an adhesive layer 6' the reinforcing fibers 2 orientated in one direction onto a supporting sheet made of reinforcing fibers 4 interwoven into a cloth, is prepared.

[0019] More specifically, as supporting sheet resin-permeable screen cloths, glass cloths or the like are

utilised. Therefore, as it will hereinafter be detailed later, said supporting sheet 4 and the reinforcing fibers 2 can be impregnated with resin, i.e. the matrix resin 6, from the side of the supporting sheet 4. The thickness of the supporting sheet 4 should be comprised within an 1~500 $\mu$ m range, preferably in a 5~50 $\mu$ m range, because the reinforcing fibers 2 should be flexible, concomitantly having a sufficient supporting strength.

[0020] In general, the adhesive agent forming the adhesive layer 6' can be any adhesive agent capable to adhere, at least temporarily, the reinforcing fibers 2 the supporting sheet 4 therebetween, however preferably an adhesive agent capable to convey, by means of the matrix 6, the reinforcing effect of the fibers to the adhesive layer as well is utilised. Accordingly, preferably a resin having a good mutual solubility with the matrix resin 6 should be utilised in the adhesive layer 6'. For instance, when using an epoxy resin as matrix resin, an epoxy-type adhesive agent is to be preferred. The thickness of the adhesive layer 6' can be selected within a 5~100 $\mu$ m range, preferably within a 10~30 $\mu$ m range, since it should temporarily adhere the reinforcing fiber 2 and the supporting sheet 4 therebetween.

[0021] The reinforcing fibers 2 are obtained by converging filaments into fiber bundles by means of a converging agent



or of a slight twisting thereof. Those bundles are lined up, and adhered, slightly scattered thereamong, onto the adhesive layer 6' by means of a downward pressure applied thereon. The reinforcing fibers 2 thus obtained, laminated in several layers by means of a twisting or converging agent and oriented in one direction, are adhered onto the supporting sheet by means of an adhesive layer 6'. Thus, the desired reinforcing fiber sheet 1 is obtained.

[0022] In this case, as shown in Fig. 3 (a), the reinforcing fiber 2 can be formed by lining up the reinforced fiber bundles 2' onto the supporting sheet 4 by means of the adhesive layer 6'. Said fiber bundles 2' are oriented in one direction and horizontally closely packed thereamong. Then, as shown in Fig. 3 (b), the lower portion of the reinforcing fiber bundles is adhered onto the supporting sheet 4<sup>1</sup> by means of the adhesive layer 6', by exerting a downward pressure onto the fiber bundles 2', thereby closely adhering the bundles without horizontal spacing thereamong onto the supporting sheet 4. Alternatively, as shown in Fig. 4 (a), the reinforcing fiber 2 can likewise be formed by lining up the reinforced fiber bundles 2' onto the supporting sheet 4 by means of the adhesive layer 6', but with the fiber bundles 2' oriented in one direction and horizontally loosely packed

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<sup>1</sup> [PUNTO TRADUZIONI'S NOTE: The original mistakenly reports the reference No. 2 ]

thereamong, and by adhering the lower portion of the bundles 2' onto the sheet 4 by exerting a downward pressure thereon, thereby forming horizontal spacing thereamong, as shown in Fig. 4 (b).

[0023] Fiber bundles 2' wherein the opening among the comrade fibers, i.e. the comrade filaments, has been carried out or not can be utilised. The amount of pressure to be exerted onto the fiber bundles can be set at will. However, when e.g. carbon fibers are utilised as reinforcing fiber 2, in case of carbon fiber bundles in which about 12000 filaments having a 5~15 $\mu$ m diameter are converged, the bundles will be pressed in order to attain an approximate horizontal width of 5 mm.

[0024] As shown in Fig. 5, a reinforcing fiber sheet 1 thus made is adhered onto a front or rear side of the fragile plate material 100. Said plate material 100 has a primer 6'', made of the same resin type of the matrix resin 6, applied thereon. The sheet 1 should face the fragile plate material 100 at the side provided with the reinforcing fibers 2. Preferably, a primer 6'' could be applied onto the fragile plate material 100 surface prior to the positioning of the reinforcing fiber sheet 1.

[0025] Furthermore, the matrix resin 6 is applied by means of a spreading roller or the like at the supporting sheet 4 side, positioned onto the outer side of the sheet 1 lying onto the fragile plate material 100. Thus, the matrix resin

6, seeps through the supporting sheet 4, until reaching the reinforcing fiber 2. Then, always maintaining the resin-impregnated reinforcing fiber sheet 1 pressed onto the fragile plate material 100 with suitable means, the matrix resin 6 is thermally hardened.

[0026] Thus, the composite plate material 100 is manufactured as shown in Fig. 1, laminating therebetween the first fiber-reinforced resin layer 102, formed impregnating with the resin 6 the reinforcing fibers 2 oriented in one direction, and the second fiber-reinforced resin layer 104, formed impregnating with the resin 6 the reinforcing fibers interwoven into a cloth, onto a side of the fragile plate material 100.

[0027] The instance in which an individual reinforcing fiber sheet 1 is laminated onto a fragile plate material has been disclosed in the preceding embodiment, however, several sheets can be laminated in order to satisfy specific needs. In this instance the laminated reinforcing fiber sheets 1 can be oriented so that the respective directions of the reinforcing fibers 2 oriented in one direction differ thereamong. Moreover, although in the present embodiment the reinforcing fiber sheet 1 was attached to the fragile plate material 100 from the side of the reinforcing fiber 2 oriented in one direction, the reinforcing fiber sheet 1 could also be attached to the fragile plate material 100 from the side of the supporting

sheet 4.

[0028] Furthermore, according to another embodiment of the present invention, initially the matrix resin 6 is applied onto the reinforcing fibers 2 oriented in one direction or onto the supporting sheet 4 of the reinforcing fiber sheet 1, by means of a suitable application device such as a spreading roller, a brush, a sprayer or the like. Then, a single, or a suitable number of, reinforcing fiber sheet 1 is attached and laminated onto the fragile plate material, which, in order to satisfy specific needs, can be provided with a primer, from the side thereof where said resin has been applied. Subsequently, the matrix resin can also be applied onto the outer surface of the reinforcing fiber sheet 1 with a hand roller or the like, and the impregnation of the sheet 1 can take place.

[0029] In the present invention, heating means can advantageously be made superfluous when a resin hardening at room temperature is utilised as matrix resin, e.g., an epoxy resin hardened at room temperature by adjusting the rate of a hardening agent.

[0030] In comparison with the known manufacture of composite plate material carried out by laminating pre-impregnated layers, the above-disclosed manufacture of a composite plate material 10 according to the present invention advantageously allows simpler pressurising and heating means of the fragile plate material 100, thereby

easing the entire process. Moreover, the reinforcing fiber sheet 1 can be fittingly applied onto the contour of the fragile plate material 100 even when the surface of the latter is curved, because it has been applied prior to the impregnation with the matrix resin 6. Hence, a good machinability, as well as a flawless positioning thereof are provided.

[0031] Hereinafter, a more detailed description of the composite plate material 10 according to the present invention will be provided.

[0032] Embodiment example 1.

A ceramic plate (600x600 mm, 4 mm thick) is utilised as fragile plate material 100, the related reinforcing fiber sheet 1 being implemented as follows:

[0033] A 30 $\mu$  wide glass cloth (product name: KS-1020, manufactured by Kanebô Co.ltd.) is utilised as the supporting sheet 4, onto which a mere 20g/m<sup>2</sup> of epoxy resin is applied as adhesive layer 6'.

[0034] As reinforcing fiber 2, PAN type 7.0 $\mu$ m diameter carbon fibers (product name T-300, manufactured by Tôre Co.ltd.) are utilised. Said carbon fibers are bundled together with 12000 filaments per bundle, and arranged onto the aforementioned supporting sheet 4 with a 4.6 mm spacing, then the reinforcing fiber bundles 2' are pressed downwards until a 5 mm horizontal width thereof is

attained, and the reinforcing fibers 2 are arranged onto the supporting sheet 4, equally spaced thereamong.

[0035] A primer is applied onto a surface of the aforementioned fragile plate material 100, then the aforementioned reinforcing fiber sheet 1 is attached onto said surface, facing the material 100 with the carbon fibers 2 of the sheet 1. Moreover, the matrix resin 6 is applied at the side the supporting sheet 4 by means of a spreading roller, impregnating it until reaching the reinforcing fibers 2. As matrix resin 6 a type of epoxy resin hardening at room temperature (product name: FR resin, manufactured by Tōnen Co.ltd) is utilised.

[0036] After 24 hours under the abovedisclosed conditions the matrix resin 6 is hardened. The reinforcing fibers/matrix resin ratios in the first and second fiber-reinforced resin layers 102, 104 of the composite plate material 100 thus made, expressed as percentage by weight, are the following:

in the first fiber-reinforced resin layer 102,  
reinforcing fibers 40%, matrix resin 60%;

in the second fiber-reinforced resin layer 104,  
reinforcing fibers 30%, matrix resin 70%;

furthermore, the thicknesses of the first and second fiber-reinforced resin layers 102, 104 are  $T_1=320\mu\text{m}$  and  $T_2=60\mu\text{m}$ , respectively.

[0037] A bending test was carried out on said composite

plate material 10 by the present inventors. Such composite plate material 10 displayed a  $2.4 \text{ kgf/mm}^2$  bending strength, i.e. 6.7 times greater than the bending strength of the 4 mm wide ceramic plate 100 ( $0.36 \text{ kgf/mm}^2$ ). Moreover, with regard to the shock resistance of the composite material, the non-reinforced ceramic plate broke, whereas the composite plate material of this embodiment, formed according to the present invention, did not.

[0038] Furthermore, the present inventors carried out a bending test of the present embodiment, slicing a 15x20 mm testing specimen of the composite plate material 10, providing the reinforcing fiber 2 longitudinally oriented in one direction to be lined up; said testing specimen was positioned onto two supporting rods having a 2 mm radius spaced of 100 mm therebetween, and a 5 mm radius head was pushed onto the median portion of said testing specimens by means of a 3.5 mm thickness Teflon plate, and pressed thereon with a 2 mm/min head speed.

[0039] Further, the present inventors carried out a shock resistance test onto the composite plate material 10, positioning it onto two supporting rods having a 2 mm radius and spaced of 100 mm therebetween, located longitudinally to the reinforcing fibers 2 oriented in one direction, and dropping a 500g steel ball from a 300 mm height onto the median section of said testing specimen.

[0040] Comparative example 1

The glass cloth utilised in the previous embodiment was attached onto a surface of the same ceramic plate material 100 of the previous embodiment, and a composite plate material was manufactured, impregnating it with the same epoxy resin of the room temperature hardening type already utilised in the previous embodiment. After 24 hours under the above conditions the matrix resin 6 was hardened.

[0041] The reinforcing fiber cloth/matrix resin ratio in the fiber-reinforced resin layer of the composite plate material thus manufactured, expressed as percentage by weight, is the following:

reinforcing fibers 40%, matrix resin 60%;

furthermore, the thickness of the fiber-reinforced composite resin layer is of 320 $\mu$ m.

[0042] Bending strength and shock resistance tests were also carried out by the present inventors on such composite plate material, adopting the same testing method of the previous embodiment. This composite plate material did not break during the shock resistance test, however, with regard to the bending strength test, it displayed only a 1.0 kgf/mm<sup>2</sup> bending strength, 2.8 times that of the single ceramic plate material (0.36 kgf/mm<sup>2</sup>), showing a reinforcing effect lower than the one displayed in the previous embodiment.

[0043] Comparative example 2

The same carbon fiber bundles utilised in the embodiment 1



were positioned, with a 4.6 mm spacing thereamong, onto the same ceramic plate material 100 of the previous embodiment, and a downward pressure was exerted onto each bundle until a 5 mm horizontal width and an equal arrangement thereamong was attained. Then the composite plate material was formed, impregnating the carbon fibers with the same epoxy resin of a type hardening at room temperature utilised in the previous embodiment. After 24 hours under the above conditions the matrix resin 6 was hardened.

[0044] The reinforcing fiber/matrix resin ratio in the fiber-reinforced resin layer of the composite plate material thus manufactured, expressed as percentage by weight, is the following:

reinforcing fibers 40%, matrix resin 60%;

furthermore, the thickness of the fiber-reinforced composite resin layer is of 320 $\mu$ m.

[0045] Bending strength and shock resistance tests were also carried out by the present inventors on this composite plate material, adopting the same testing method of the previous embodiment. With regard to the bending strength test, this composite plate material displayed a (2.5 kgf/mm<sup>2</sup>) bending strength , 6.9 times that of the non-reinforced ceramic plate material (0.36 kgf/mm<sup>2</sup>), but as it broke during the shock resistance test, it did not provide a satisfactory reinforcing effect.

[0046]

[EFFECT OF THE PRESENT INVENTION] The composed plate material according to the present invention manufactured as hereto disclosed can display a sufficient shock resistance and bending strength even when the thickness of a fragile plate material is not larger than 5 mm, and improves the handling convenience and reduces the weight. Moreover, by virtue of the manufacture of the composite plate material according to the present invention, the heating and pressurising means are simplified, thereby allowing a highly versatile manufacture, that can easily be implemented even in case of curved fragile plate materials.

[BRIEF EXPLANATION OF THE DRAWINGS]

[Fig. 1] is a sectional view of the structure of the composite plate material of an embodiment according to the present invention.

[Fig. 2] is a sectional view of the structure of the reinforcing fiber sheet utilised in the manufacture of the composite plate material according to the present invention.

[Fig. 3] is a sectional view of the structure of the reinforcing fiber sheet, illustrating the manufacture thereof.

[Fig. 4] is a sectional view of the structure of the reinforcing fiber sheet, illustrating the manufacture thereof.

[Fig. 5] is a sectional view of the structure of the

composite plate material according to the present invention, illustrating the manufacture thereof.

[REFERENCE NUMBERS]

- 1 ..... Reinforcing fiber sheet
- 2 ..... Reinforcing fibers oriented in one direction;
- 4 ..... Reinforcing fiber cloth (supporting sheet);
- 6 ..... Matrix resin;
- 6' ..... Adhesive layer;
- 6" ..... Primer;
- 100 ..... Fragile plate material;
- 102 ..... First fiber-reinforced resin layer;
- 104    Second fiber-reinforced resin layer;